

PTO 98-3783

CY=JP DATE=19960319 KIND=A
PN=08-075292

OPERATION METHOD OF ABSORBING TYPE REFRIGERATOR
AND ABSORBING LIQUID FOR ABSORBING TYPE REFRIGERATOR
[Kyushushiki reitokino untenhoho oyobi kyushureitokiyo kyushueki]

Hidemasa Nonaka

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. AUGUST 1998

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	08075292
DOCUMENT KIND	(12):	A
PUBLICATION DATE	(43):	19960319
PUBLICATION DATE	(45):	
APPLICATION NUMBER	(21):	06209439
APPLICATION DATE	(22):	19940902
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	F25B 15/00 15/06 47/00 C09K 5/04
DOMESTIC CLASSIFICATION	(52):	
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
INVENTORS	(72):	NONAKA, HIDEMASA
APPLICANT	(71):	OSAKA GAS CO LTD
TITLE	(54):	OPERATION METHOD OF ABSORBING TYPE REFRIGERATOR AND ABSORBING LIQUID FOR ABSORBING TYPE REFRIGERATOR
FOREIGN TITLE	[54A]:	KYUSHUSHIKI REITOKINO UNTENHOHO OYOBI KYUSHUREITOKIYO KYUSHUEKI

[Title]

OPERATION METHOD OF ABSORBING TYPE REFRIGERATOR AND
ABSORBING LIQUID FOR ABSORBING TYPE REFRIGERATOR

[Summary]

[Purpose]

Pertaining to an absorbing type refrigerator which uses lithium bromide solution as an absorbing liquid, this invention provides the operation method by which the absorbing type refrigerator is operated, keeping hydrogen gas from being generated due to local or total corrosion when it contains devices made of stainless steel, and the absorbing liquid for the absorbing type refrigerator.

[Constitution]

Pertaining to an absorbing type refrigerator in which lithium bromide (LiBr) solution is used as an absorbing solution and devices made of stainless steel are included, it is operated using the absorbing liquid in which the lithium hydroxide (LiOH) density is 0.01~0.3N, more than 250ppm of sodium sulfite (Na_2SO_3) or sodium hydrogen-sulfite (NaHSO_3) converted in sodium sulfite equivalent, and 200~2000ppm of antimony chloride (SbCl_3) or

*Numbers in the margin indicate pagination in the foreign text.

antimony oxide (Sb_2O_3) converted in antimony chloride equivalent are included.

[Claims]

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[Claim 1]

Pertaining to an operation method of an absorbing type refrigerator which uses lithium bromide (LiBr) solution as an absorbing liquid, an operation method of an absorbing type refrigerator in which an alkaline metal hydroxide compound and an antimony compound are added to the aforementioned absorbing liquid when the aforementioned refrigerator contains the devices made of stainless steel.

[Claim 2]

An operation method of an absorbing type refrigerator described in Claim 1, in which the aforementioned alkaline metal hydroxide compound is lithium hydride whose density is $0.01\sim 0.3\text{N}$, and the aforementioned antimony compound is either antimony chloride (SbCl_3) or antimony oxide (Sb_2O_3) whose density is $200\sim 1800\text{ppm}$ when converted in antimony chloride (SbCl_3) equivalent.

[Claim 3]

Pertaining to an operation method of an absorbing type refrigerator which uses lithium bromide (LiBr) solution as an absorbing liquid, when the aforementioned refrigerator contains the devices made of stainless steel, the operation method of an

absorbing type refrigerator in which an alkaline metal hydroxide compound, oxoacid salt which is reducible and has sulfur as a central atom and a metal compound whose hydrogen overvoltage is large are added to the aforementioned absorbing liquid.

[Claim 4]

An operation method of an absorbing type refrigerator described in Claim 3 in which the metal compound whose hydrogen overvoltage is large is an antimony compound.

[Claim 5]

An operation method of an absorbing type refrigerator described in Claim 4, in which the aforementioned alkaline metal hydroxide compound is lithium hydride whose density is 0.01~0.3N, the aforementioned oxoacid salt is either sodium sulfite (Na_2SO_3) or sodium hydrogen sulfite (NaHSO_3) and its density is more than 250ppm when converted in sodium sulfite (Na_2SO_3) equivalent, and the aforementioned antimony compound is either antimony chloride (SbCl_3) or antimony oxide (Sb_2O_3) and its density is 200~2000ppm when converted in antimony chloride (SbCl_3) equivalent.

[Claim 6]

Pertaining to the absorbing liquid for an absorbing type refrigerator which uses lithium bromide (LiBr) solution as an absorbing liquid and contains the devices made of stainless steel, an absorbing liquid for an absorbing type refrigerator in which the density of lithium hydride (LiOH) is 0.1~0.3N and

200~1800ppm of antimony chloride (SbCl_3) or antimony oxide (Sb_2O_3) when converted in antimony chloride (SbCl_3) equivalent.
[Claim 7]

Pertaining to the absorbing liquid for an absorbing type refrigerator which uses lithium bromide (LiBr) solution as an absorbing liquid and contains the devices made of stainless steel, an absorbing liquid for an absorbing type refrigerator in which the density of lithium hydroxide (LiOH) is 0.1~0.3N, and more than 250ppm of sodium sulfite (Na_2SO_3) or sodium hydrogen sulfite (NaHSO_3) when converted in sodium sulfite (Na_2SO_3) equivalent, and 200~2000ppm of antimony chloride (SbCl_3) or antimony oxide (Sb_2O_3) when converted in antimony chloride (SbCl_3) equivalent are included.

[Details]

[0001] [Industrial Utilization]

This invention pertains to an operation method of an absorbing type refrigerator which uses lithium bromide (LiBr) solution as an absorbing liquid of an absorbing type air conditioner and contains the devices made of stainless steel, and an inhibitor which prevents corrosion of device materials when added to the absorbing liquid.

[0002] [Conventional Technology]

In recent years, more and more studies have been conducted to adopt an absorbing type refrigerator which uses the

aforementioned absorbing liquid as a working medium in home heaters and air conditioners. An absorbing type refrigerator is generally oversized; and to solve the problems of the reduction of the refrigeration efficiency and corrosion due to the gas generated inside, a good working condition is maintained by placing an air removing device inside or by checking the conditions of the absorbing liquid frequently. In order to utilize such an absorbing type refrigerator in home heaters and air conditioners, the size of the refrigerator itself needs to be reduced; and for that, the size of the air removing device needs to be minimal or it needs to be eliminated. In addition, it is desirable that the refrigerator is maintenance free. For such reasons, more attempts are made to adopt stainless steel for the composing devices of an absorbing type refrigerator.

[0003]

Conventionally, metal materials such as soft steel, copper and brass are used as the material for composing devices of an absorbing type refrigerator. The corrosion inhibiting technology for such materials are relatively advanced; however, such technology for stainless steel is not yet established. Therefore, the inventors have suggested an idea in which by adding a reducer, the natural corrosion electric potential (E_{corr}) of stainless steel is reduced, and local corrosion in lithium bromide solution is prevented (Tokugan #05268516).

[0004] [Problems to Be Solved]

When the natural corrosion electric potential (E_{corr}) is reduced as explained above, local corrosion is prevented; however, hydrogen type corrosion (total corrosion) takes place easily. When hydrogen gas is generated, the vacuum level is reduced, which leads to the reduction of the refrigeration ability, which interferes with its function as a heater or an air conditioner.

[0005]

Therefore, the purpose of this invention is, pertaining to the aforementioned absorbing type refrigerator, to provide the operation method by which the absorbing type refrigerator is operated, keeping hydrogen gas from being generated due to local or total corrosion when it contains devices made of stainless steel, and the absorbing liquid for the absorbing type refrigerator.

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[0006] [Solutions]

The first characteristic means of the operation method of an absorbing type refrigerator which uses lithium bromide (LiBr) solution as an absorbing liquid as described in Claim 1 is that an alkaline metal hydroxide compound and an antimony compound are added to the aforementioned absorbing liquid when the aforementioned refrigerator contains the devices made of stainless steel. Furthermore, in the aforementioned first

characteristic means, it is desirable that the aforementioned alkaline metal hydroxide compound is lithium hydride whose density is 0.01~0.3N, and the aforementioned antimony compound is either antimony chloride (SbCl_3) or antimony oxide (Sb_2O_3) whose density is 200~1800ppm when converted in antimony chloride (SbCl_3) equivalent, which is the second characteristic means of this invention. Furthermore, the third characteristic means of an operation method of an absorbing type refrigerator which uses lithium bromide (LiBr) solution as an absorbing liquid as described in Claim 3 is that when the aforementioned refrigerator contains the devices made of stainless steel, the operation method of an absorbing type refrigerator in which an alkaline metal hydroxide compound, oxoacid salt which is reducible and has sulfur as a central atom and a metal compound whose hydrogen overvoltage is large are added to the aforementioned absorbing liquid. Furthermore, in the aforementioned third characteristic means, it is desirable that the metal compound whose hydrogen overvoltage is large is an antimony compound, which is the fourth characteristic means of this invention. Furthermore, in the aforementioned fourth characteristic means, it is desirable that the aforementioned alkaline metal hydroxide compound is lithium hydride whose density is 0.01~0.3N, the aforementioned oxoacid salt is either sodium sulfite (Na_2SO_3) or sodium hydrogen sulfite (NaHSO_3) and its density is more than 250ppm when converted in

sodium sulfite (Na_2SO_3) equivalent, and the aforementioned antimony compound is either antimony chloride (SbCl_3) or antimony oxide (Sb_2O_3) and its density is 200~2000ppm when converted in antimony chloride (SbCl_3) equivalent, which is the fifth characteristic means of this invention. The first characteristic structure of the absorbing liquid for an absorbing type refrigerator which uses lithium bromide (LiBr) solution as an absorbing liquid and contains the devices made of stainless steel as described in Claim 6 is that the density of lithium hydride (LiOH) is 0.1~0.3N and 200~1800ppm of antimony chloride (SbCl_3) or antimony oxide (Sb_2O_3) when converted in antimony chloride (SbCl_3) equivalent. Furthermore, the second characteristic structure of the absorbing liquid for an absorbing type refrigerator which uses lithium bromide (LiBr) solution as an absorbing liquid and contains the devices made of stainless steel as described in Claim 7 is that the density of lithium hydride (LiOH) is 0.1~0.3N, and more than 250ppm of sodium sulfite (Na_2SO_3) or sodium hydrogen sulfite (NaHSO_3) when converted in sodium sulfite (Na_2SO_3) equivalent, and 200~2000ppm of antimony chloride (SbCl_3) or antimony oxide (Sb_2O_3) when converted in antimony chloride (SbCl_3) equivalent are included. Their effects are as follows.

[0007] [Effect]

As explained above, total corrosion takes place on stainless steel, generating hydrogen gas. For inhibitors, the inventors suggests the combination of alkali and an antimony compound (Claims 1, 2 and 6) and the combination of alkali, oxoacid salt which is reducible and has sulfur as a central atom as a reducer and the metal whose hydrogen overvoltage is large (Claims 3, 4, 5, 7). In the former combination, by combining alkali and an antimony compound, the system is maintained reducible (Since $\text{SbCl}_3(\text{Sb}^{3+})$ is slightly reducible, it shows the reducibility even without a reducer (oxoacid salt which is explained in the latter combination)), the stainless steel surface is plated with antimony, which inhibits hydrogen gas from being generated. In the latter combination, by the combination of alkali and oxoacid salt which is reducible and has sulfur as a central atom as a reducer, the system is maintained reducible, and the stainless steel surface is plated with the metal whose hydrogen overvoltage is large, which inhibits hydrogen gas from being generated. Thus, in this invention, the system is maintained reducible, and by the plating of the metal whose hydrogen overvoltage is large, corrosion on stainless steel is inhibited. Hereafter, this invention is explained using antimony which can represent the metals whose hydrogen overvoltage is large as an example.

[0008]

When antimony is added to the lithium bromide solution, since the system is in the reducible atmosphere (automatically in the former combination; by adding a specific reducer in the latter combination), antimony metal is plated on the stainless steel surface (this is confirmed by inventors by experiments). Since antimony is a kind of metal in which the cathode reaction of $\text{H}^+ + \text{e} \rightarrow 1/2\text{H}_2$ is difficult to achieve (the hydrogen overvoltage is large), the total corrosion reaction of $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}$ which pairs with the hydrogen generating reaction is difficult to achieve (works as the cathode reaction inhibiting type inhibitor). Therefore, total corrosion and hydrogen gas generation are inhibited (needless to say, local corrosion is inhibited as well). Therefore, with stainless steel, this invention inhibits hydrogen gas from being generated by adding the metal whose hydrogen overvoltage is large while keeping its electric potential lower.

[0009]

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Hereafter, the characteristic means of the operation method of the aforementioned absorbing type refrigerator and the characteristic structures of the absorbing liquid are explained.

When the first characteristic means of this invention is selected, as explained above, total corrosion (generation of hydrogen gas) as well as local corrosion can be inhibited by the

combination of an antimony compound and alkali, utilizing the reducibility of antimony ions. When the second characteristic means of this invention is selected, as shown in Fig. 1 (b) which will be explained later, the refrigerator is operated with the corrosion and the hydrogen gas generation more effectively controlled than when antimony chloride is not added.

[0010]

When the third characteristic means of this invention is selected, as explained above, the reducibility of the system is maintained by oxoacid salt which is reducible and has sulfur as a central atom, preventing the problem of corrosion; furthermore, by adding the metal compound whose hydrogen overvoltage is large, the stainless steel surface is plated with the metal, which inhibits total corrosion (hydrogen gas generation). At this time, alkali adjusts basicity. When the fourth characteristic means of this invention is selected, by using an antimony compound whose hydrogen overvoltage is especially large, corrosion is inhibited effectively; for example, as shown in Fig. 1 (a), corrosion and hydrogen gas generation are inhibited in a relatively large density range. This makes the maintenance and control of the absorbing liquid easier, which is effective to materialize the maintenance-free machine. When the fifth characteristic means of this invention is selected, as shown in Fig. 1 (a) which will be explained later, the refrigerator is

operated with the corrosion and the hydrogen gas generation more effectively controlled than when antimony chloride is not added. When the absorbing liquid which has the first characteristic structure of this invention is used, by the same effect explained in the second characteristic means of this invention, local corrosion and hydrogen gas generation can be inhibited effectively with an absorbing type refrigerator containing the devices made of stainless steel. When the absorbing liquid which has the second characteristic structure of this invention is used, by the same effect explained in the fifth characteristic means of this invention, local corrosion and hydrogen gas generation can be inhibited effectively with an absorbing type refrigerator containing the devices made of stainless steel.

[0011] [Effects]

Therefore, pertaining to an absorbing type refrigerator which uses lithium bromide solution as an absorbing liquid, this invention provides the operation method by which the absorbing type refrigerator is operated, keeping hydrogen gas from being generated due to local or total corrosion when it contains devices made of stainless steel, and the absorbing liquid for the absorbing type refrigerator.

[0012] [Examples]

To check the corrosion condition of the stainless steel in the lithium bromide solution, an immersion experiment is conducted. Hereafter, the experiment conditions are listed.

Test piece

Material: High purity ferrite stainless steel

Shape: L50mm x W80mm x Thickness t2mm

Number: Five (5) test pieces are tested under the same conditions.

Solution Lithium bromide solution

Density: 60% (approx.)

Temperature: 157°C

LiOH is added to adjust the basicity (0.01~0.3N)

Testing time 720 hours

The results of the experiment under the above conditions are shown in Fig. 1. Figure 1 (a) shows the results when sodium sulfite (Na_2SO_3) which is an effective reducer is added, while Fig. 1 (b) shows the results when it is not added. The amount of sodium sulfite to add is 250ppm or more (explained in detail in Tokugan #05268516). In each figure, the horizontal axis shows the amount of antimony chloride (SbCl_3) to add; the vertical axes show the depth of the largest corroded area (μm) on the left side, and the amount of generated hydrogen gas (Nml) per 1.6m^2 on the right side. In both figures, the solid lines show the depth

of the largest corroded area out of the five pieces used for the test, and the broken lines show the amount of generated hydrogen gas.

[0013]

When Figs. 1 (a) (b) are compared, it is clear that in both cases, the ones to which sodium sulfite is added show the better results in both corrosion and hydrogen gas generation. Furthermore, as shown in Figs. 1 (a) (b), when antimony chloride is added within a certain density range, corrosion and hydrogen gas generation are almost zero. The ranges are 250~1000ppm for the one to which sodium sulfite is added, and 250~500ppm for the one to which sodium sulfite is not added. Furthermore, the ranges of the amount to add to improve corrosion and hydrogen gas generation are 200~2000ppm for the one to which sodium sulfite is added, and 200~1800ppm for the one to which sodium sulfite is not added. Therefore, by setting the density of antimony chloride, corrosion and hydrogen gas generation can be inhibited.

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[0014]

Furthermore, the conditions of stress corrosion cracking (SCC) of austenite stainless steel which is used with the aforementioned high purity ferrite stainless steel for the composing devices of an absorbing type refrigerator are checked. The structure of the experiment device for stress corrosion cracking (SCC) is shown in Fig. 2 (in the following description,

the numbers of the responding materials are shown in the figure, and the numbers are noted next to the material names).

Hereafter, the experiment conditions are listed.

Test piece	1
Materials	Austenite stainless steel
Shape	Double-U-bent (1a), single-U-bent with a soldering area (1b).

The "double-U-bent" (1a) is, as shown in Fig. 2, the two pieces (2, 3) are layered together which are clamped together with a clamping fixture (4) composed of bolts and nuts. The "single-U-bent" has a single piece (20). As shown in Fig. 2, the "single-U-bent" (1b) has welded areas (5). For experiments, as shown in Fig. 2, two pairs of the "double-U-bent" (1a) and one pair of the "single-U-bent" (1b) are used.

Solution 6	Lithium bromide solution
	Density: 60% (approx.)
	Temperature: 157°C
	LiOH is added to adjust the basicity (0.01~0.3N range)
	Sodium sulfite: Density 2000ppm
	(Items with or without it)

Antimony chloride: Density 500ppm

Testing time: 1000 hours (1 month)

The experiment results are shown in Table-1. The left side of the table shows the results with the one to which sodium sulfite is added responding to Fig. 1 (a), and the right side shows the results with the one to which a reducer is not added responding to Fig. 1 (b). The upper rows of the table (noted as "vacuum" in the table) show the results when there is a vacuum (to be precise, a small amount of oxygen remains) when the absorbing type refrigerator is working normally; the lower rows (noted as "air" in the table) show the results when there is an air leak. The word "half" in the table means the test piece which is half immersed, while the word "all" in the table means the test piece which is entirely immersed.

[0015]

[Table 1]

SCC Observation Results

1.5 months, Double-U, Welded U-bent

With Na ₂ SO ₃			Without Na ₂ SO ₃	
	Out Out In In Weld		Out Out In In Weld	
Half	X O O O O	Vacuum	X X X O X	Half
All	O O O O O	Vacuum	O O O O O	All
Half	X X X X X	Air	X X X X X	Half
All	O O O O O	Air	O O O O O	All

In the table, "Out", "In", "Weld", "O", and "X" stand for the following:

"Out": Outside of the "double-U-bent" (1a)

"In": Inside of the "double-U-bent" (1a)

"Weld": The "single-U-bent" (1b) with welded areas

"O": No cracks

"X": Cracks

[0016]

As a result, it is clear that sodium sulfite (Na₂SO₃) and antimony chloride (SbCl₃) are effective for the stress corrosion cracks (SCC) of SUS316L (When sodium sulfite (Na₂SO₃) and antimony chloride (SbCl₃) are not added, no stress corrosion cracks (SCC) are resulted with the half-immersion and the all-immersion).

[0017]

In a double effect absorbing type refrigerator selected as an example of an absorbing type refrigerator, the following two operation experiments (1500 hours of testing time) are conducted under the following conditions.

Absorbing liquid ingredients	1st example	2nd example
Lithium bromide density	60%	60%
LiOH density	0.06N	0.06N
Na ₂ SO ₃ density	2000ppm	2000ppm
Sb compound density	SbCl ₃ 500ppm	Sb ₂ O ₃ 640ppm

The results of the operations of the double effect absorbing type refrigerator under the aforementioned conditions are explained along with the results of such with the conventional technology (the one to which only alkali (LiOH) is added, and the one to which alkali and sodium sulfite (Na₂SO₃) are added) as follows:

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	Amount of hydrogen gas	Local corrosion
1st example	20cc (approx.)	None
2nd example	20cc (approx.)	None
Alkali (LiOH) added (no O ₂)	400cc	None
Alkali & Na ₂ SO ₃ added	1000cc	None

As explained above, in this invention, by combining alkali, a reducer and a metal compound whose hydrogen overvoltage is large (antimony in this example), corrosion on stainless steel can be inhibited effectively in the areas of local corrosion and hydrogen gas generation.

[0018] (Another example)

In the aforementioned examples, the combination of alkali (represented by LiOH) and an antimony compound (represented by SbCl₃ or Sb₂O₃) (we call it the first combination) and the combination of alkali (represented by LiOH), a reducer (represented by Na₂SO₃ or NaHSO₃) and an antimony compound (represented by SbCl₃ or Sb₂O₃) (we call it the second combination) are explained. For each combination, the following substances work well as an inhibitor.

1. The first combination: Since no reducer is added in this combination, the substance which is added along with alkali needs to be reducible when resolved. Therefore, in this combination, only an antimony compound works well. As such a compound, antimony chloride (SbCl₃), antimony oxide (Sb₂O₃), antimony bromide (SbBr₃), antimony iodide (SbI₃) and the like can be used. For alkali, "LiOH" is used generally; however, since it is for adjusting the basicity, any alkali hydroxide metal compound can be used.

2. The second combination: In this combination, to form a thin film on stainless steel with an added reducer, the substance which is added along with alkali needs to have a large hydrogen overvoltage. For such a metal compound, in addition to the aforementioned antimony compounds, lead compounds (lead oxide, etc.), cadmium compounds (cadmium chloride, etc.), tin compounds (cadmium chloride, etc.), zinc compounds (zinc chloride, etc.), indium compounds (indium chloride, etc.), tellurium compounds (tellurium chloride, etc.), bismuth compounds (bismuth chloride, etc.) and the like can be used. Furthermore, the case sodium sulfite is used as a reducer was explained earlier; however, in this invention, sodium hydrogen sulfite (NaHSO_3), sodium disulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium thiosulfite ($\text{Na}_2\text{S}_2\text{O}_3$) work effectively as well. Furthermore, lithium salt and kalium salt work effectively as well. Therefore, these are called the oxoacid salt which is reducible and has sulfur as a central atom. It seems as though any reducer can be used as a substance added to the lithium bromide solution to work as an oxoacid salt for the purpose of controlling the oxidation; however, according to the experiments by the inventors, the aforementioned purpose cannot be attained with hydrazine and the like. It is decomposed at the higher temperature to generate nitrogen gas and ammonia gas, therefore, it is not appropriate for the absorbing type refrigerator. For alkali, "LiOH" is used generally; however,

since it is for adjusting the basicity, any alkali hydroxide metal compound can be used.

[Figures]

[Figure 1]

The figure showing the correlation between the added amount of antimony chloride, the depth of the largest corrosion and the amount of hydrogen gas generated.

[Figure 2]

The figure showing the structure of the autoclave testing equipment for the "SCC" test.

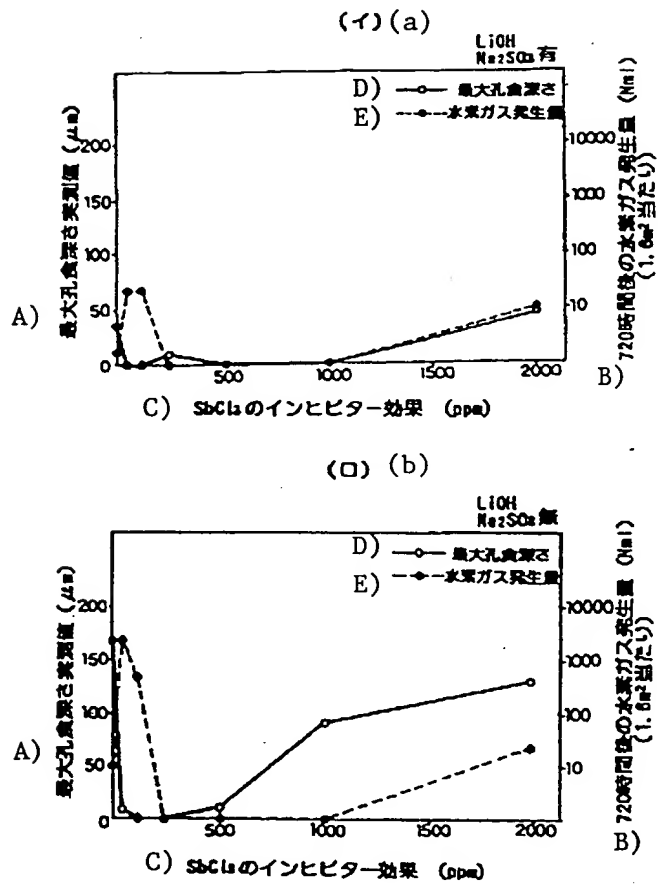
[Figure 1 (a)]

Key: A) Depth of the largest corrosion (μm); B) Amount of hydrogen gas generated in 720 hours (Nml) (per 1.6m^2); C) Inhibiting effect of SbCl_3 (ppm); D) Depth of the largest corrosion; E) Amount of hydrogen gas generated in 720 hours (Nml) (per 1.6m^2)

[Figure 1 (b)]

Key: A) Depth of the largest corrosion (μm); B) Amount of hydrogen gas generated in 720 hours (Nml) (per 1.6m^2); C) Inhibiting effect of SbCl_3 (ppm); D) Depth of the largest corrosion; E) Amount of hydrogen gas generated in 720 hours (Nml) (per 1.6m^2).

【図1】 [Figure 1]



【図2】 [Figure 2]

